

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor: ARAUJO, R. J. et al.

Serial No: 09/930,718

Group Art Unit: 1755

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Examiner: BOLDEN, Elizabeth A

Title: HIGH SILVER BOROSILICATE
GLASSES

DECLARATION

UNDER 37 C.F.R. § 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450DECLARATION UNDER 37 C.F.R. § 1.132
BY ROGER J. ARAUJO

Sir;

I, Roger J. Araujo, residing at 5 Seneca Drive, Horseheads, New York, declare:

1. I obtained a Ph.D. degree in Physical Chemistry from Brown University in 1962.
2. In 1961, I joined Corning Incorporated as a research scientist.
3. I am a member of the American Chemical Society, the Materials Research Society, Sigma Xi, and am a Fellow of the American Ceramic Society. I served as President of the Corning Chapter of Sigma Xi and as President of the Corning Section of the American Chemical Society. I was awarded the Sullivan Award in 1993 by the Corning Chapter of the American Chemical Society for my research and development work on photochromic glasses.
4. I have been engaged in researching, inventing, developing and producing glass and glass-ceramic materials and products since I joined Corning Incorporated.
5. As a result of my work in the field of glass and glass-ceramic material science and technology, I was granted US 35 patents and was the author or co-author of more than 60 related papers. In the latter half of my career I have studied statistical mechanical models of phase separation in silicate glasses, the thermodynamics of ion exchange, hydrogen aging and radiation damage in optical fibers, colorless glasses containing silver introduced by ion exchange, gaseous inclusions in glass melts, and excimer laser radiation damage in silica and in

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multicomponent glasses. A list of US patents granted to and publications (co)authored by me is attached to this Declaration as Annex 1.

6. I am a joint inventor of the above-captioned patent application.

7. I have reviewed the Rindone paper (G.E. Rindone, "The Spontaneous Growth of Silver Films on Glasses of High Silver Content," Journal of the Society of Glass Technology, Volume XXXVII, pages 124-28 (June 1953) (hereafter Rindone)) the Examiner relied on as the primary reference in her rejections in the outstanding Office action in the above-captioned application.

According to my expertise in glass science and technology, it is my understanding that there is no suggestion in the Rindone paper that high silver can be obtained in a glass that contains a high enough level of silica to produce a chemically durable glass. Although Rindone discloses a glass composition range, it gives no hint about how the limits depend on the other components. For example, Rindone mentions that silver oxide in the range of 5 to 60 wt% leads to film formation. It also mentions limits of silica from 0 to 60 wt%. That would seem to imply that a glass containing 60 wt% silica and 5% silver could be made. Rindone gives no hint about the conditions that would make this possible. Rindone certainly does not publish the composition of any borosilicate glass. In fact, regarding glasses containing silica, what is mentioned in Rindone is a silica glass containing 0.2% silver was made which produced metallic silver film on its surface. 0.2% by weight is a long way down from 2 cation percent of silver. In fact, many glasses can be made with that level of silver. All these low-level silver glasses differ substantially from what is claimed in claim 1, as amended, in the present application.

8. The glasses as taught in Rindone are prone to metallic silver film formation on the surface when exposed to water vapor, especially when subjected to light radiation at the same time. According to my expertise, these glasses thus do not have the chemical durability required for many applications where the glass is exposed to ambient air.

9. I have conducted an experiment to test the chemical durability of the glass of the present invention in the presence of water vapor. The experiment procedure was as follows:

A glass of the present invention having the following composition was melted in a crucible on August 8, 2002:

Component		SiO ₂	Al ₂ O ₃	B ₂ O ₃	Ag ₂ O
Percentage	mol	45	13	16	26
	cation	34.88	20.16	24.81	20.16

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A glass plate having the size of 17x9.5x1.8 cm was prepared from the melt and annealed. The glass plate was transparent. The glass was placed in ambient air for over a year, during which it was subjected to water vapor in the ambient air, as well as natural daylight and/or artificial room light generated by incandescent and/or fluorescent lamps. From March 3 to March 8, 2004, it was subjected to UV radiation at 366 nm for a week in ambient air. Until the date of signing this declaration, no metallic film has formed on the surface of the plate. The glass plate remains transparent to visible light.

This demonstrates that the high silver aluminoborosilicate glass as claimed in claim 1, as amended, of the present application, is stable in the presence of water vapor and light radiation as short as 366 nm, contrary to the glasses as taught in Rindone.

10. I have conducted another experiment to demonstrate that many glasses falling within the glass composition range taught in Rindone, page 125, lines 5-12, but outside of the compositional range of claim 1, as amended, of the present application, do not possess the chemical durability to withstand a molten salt bath used in an ion-exchange process. The procedure of the experiment was as follows:

Five glasses (sample Nos. 1-5) were melted in laboratory crucibles. The compositions of the glasses, in weight percentage and cation percentage, are reported in CHART I and CHART II, respectively. Clearly, sample Nos. 1-5 have compositions falling within the glass composition range taught in Rindone but outside of the glass composition range of the present invention.¹

The melted glasses were poured to form patties. The appearances of the patties, after annealing and cooling, were observed. Subsequently, slabs broken from the annealed patties for sample Nos. 1-3 and 5 were placed into 450 °C NaNO₃ bath for 1 hour where ion-exchange took place. Then they were taken out of the bath and observed for changes in appearances.

¹ In page 125, lines 5-12, Rindone specifies the glass studied in the article as having the following composition range in weight percentage:

Ag ₂ O.....	5 to 60
B ₂ O ₃	0 to 85
SiO ₂	0 to 60
Al ₂ O ₃	0 to 20.

Yet, claim 1 of the present application, as amended herein, is directed to a glass having the following composition, in cation percentage:

SiO ₂	15-60
Al ₂ O ₃	10-30
B ₂ O ₃	10-45
Ag ₂ O.....	8-25.

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CHART I

	Wt % of Sample No.				
	1	2	3	4	5
SiO ₂	0		10	30	30
Al ₂ O ₃		10			10
B ₂ O ₃	80	70	70	50	40
Ag	20	20	20	20	20

CHART II

	Cation % of Sample No.				
	1	2	3	4	5
SiO ₂	0	0	7.1	23.8	25.2
Al ₂ O ₃	0	8.2	0	0	9.8
B ₂ O ₃	93.0	84.5	85.5	68.0	56.7
Ag	7.0	7.2	7.3	8.2	8.3

Before ion-exchange, glasses 1, 2, 3 and 5 were observed to be transparent and colorless, yet glass 4 was white opaque. This indicates that sample No. 4 glass is not fit for the production of lens for transmitting visible light. For this reason, glass sample No. 4 was not tested in the molten NaNO₃ salt batch. Brown surface stains were observed on the surface of glass Sample No. 1 before ion-exchange. After placing on a piece of paper for a week in ambient air, glass No. 1 reacted badly with the supporting paper. This indicates that glass No. 1 may be hygroscopic. Before ion-exchange, purple brown stains were observed on the surface of glass Sample No. 2. Silver slugs in sizes of about 3 cm were observed in glass sample No. 2 as well. Before ion-exchange, some streaks were observed in glass sample No. 3. Silver slugs of about 8 cm size were observed. After placed in ambient air for a week, the glass sample No. 3 reacted with supporting paper slightly. No surface stain was observed on the surface of glass sample No. 5 before ion-exchange. However, multiple small silver slugs were observed inside glass No. 5. Because of the poor chemical stability of glass Nos. 1 and 3 in ambient air, the surface stains on and/or the silver slugs in glass No. 2, 3 and 5, they cannot be used for gradient index lenses.

After ion-exchange, the surfaces of glass sample Nos. 1-3 were observed to have been severely attacked. Glass Sample Nos. 1-3 became opaque. On the surface of glass samples 1-3, large area brown stains were observed. A plurality of cracks formed in sample No. 1 as a result of the ion-exchange. Sample No. 2 broke into two pieces due to a major crack formed during the molten batch treatment. Glass sample No. 5 was also attacked on the surface. Multiple white attack marks were observed.

This Example clearly shows that the above glass sample Nos. 1-5, having compositions falling within the range taught in Rindone, but outside of the claimed range of claim 1, as amended, of the present application, do not have the chemical durability to withstand the ion-

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exchange conditions. According to my expertise, these Rindone glasses thus cannot be made into glasses suitable for use in gradient index lenses by ion-exchange them in a molten salt bath.

11. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 38 U.S.C. § 1001, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

March 18, 2004
Date

Roger J. Araujo
Roger J. Araujo (Signature)

<p>CERTIFICATE OF MAILING (37 CFR 1.8a)</p> <p>I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on:</p> <p><u>3-19-04</u></p> <p><u>Colleen E. Donerty</u> Colleen E. Donerty</p>
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Annex 1

List of US Patents Granted to Dr. Roger J. Araujo²

Patent No.	Issue Date	Title
3,325,299	June 13, 1967	Photochromic Glass Article
3,328,182	June 27, 1967	Photochromic Glass Article
3,540,793	November 17, 1970	Photochromic Polarizing Glasses
3,630,765	Feb 24, 1971	Photochromic Glass for Optical Fiber Fabrication
3,649,311	March 14, 1972	Colorless Heat Absorbing Glass
3,653,863	April 4, 1972	Photochromic Polarizing Glasses
3,703,388	November 21, 1972	High Refractive Index Photochromic Glasses
3,784,386	January 8, 1974	Cladding Glass for Photochromic Optical Fibers
3,923,529	December 2 1975	Sodalite Glass Fluorescent Articles
3,981,707	September 21, 1976	Fluorine Outdiffused Optical Device
4,125,404	November 14, 1978	Photochromic Glasses Exhibiting Dichroism and Color Adaptation
4,125,405	November 14, 1978	Dichroic Birefringent Glass Articles Produced by Optical Alteration of Additively Colored Glasses
4,166,745	September 4, 1979	Index Corrected Copper-Cadmium Halide Photochromic Glasses
4,210,386	July 1, 1980	Fluorine Outdiffused Optical Device
4,405,672	September 20, 1983	Composite Photochromic Glass
4,439,528	March 27, 1984	Spontaneous Opal Glass
4,549,894	October, 1985	UV Absorbing, Low Silver Photochromic Glass
4,980,310	December 25, 1990	High Refractive Index Photochromic Glasses
5,007,948	April 16, 1991	Colorless Silver Glasses by Ion Exchange
5,192,402	March 9, 1993	Method of Dealkalizing Glass
5,212,120	May 18, 1993	Photosensitive Glass
5,281,562	January 25, 1994	Ultraviolet Absorbing Glasses
5,322,819	June 21, 1994	Ultraviolet Absorbing Glasses
5,430,573	July 4, 1995	UV Absorbing Polarizing Glass
5,517,356	May 14, 1996	Glass Polarizer for Visible Light
5,541,142	July 30, 1996	Color Filter by Precipitation of Cu ₂ O
5,578,103	November 26, 1996	Alkali Metal Migration Control
5,616,159	April 1, 1997	Fused Silica Resistance to Optical Damage
5,625,427	April 29, 1997	Ophthalmic Lens
5,668,067	September 16, 1997	Fused Silica Resistance to Optical Damage
5,674,790	October 7,	Strengthening Glass by Ion Exchange

² There may be co-inventors in these patents.

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	1997	
5,735,921	April 7, 1998	Reducing Laser Induced Damage in Silica
6,001,755	December 14, 1999	UV Absorbing Liquid
6,124,038	September 26, 2000	Strong UV Absorbing Glass
6,403,508 B1	June 11, 2002	Fused Silica with Constant Induced Absorption

List of Publications by Dr. Roger J. Araujo

Journal & page	Year	Coauthors	Subject
J. Chem. Phys. 1229	1966	No	Viscosity
Glass Industry 687	1967	Yes	Photochromic Glass
Applied Optics 777	1968	Yes	Polarizing Glass
Applied Physics 781	1968	No	Darkening Kinetics
Advances In Display	1968	No	Photochromic Glass
"Reactivity in Solids" 707	1969	No	Darkening Kinetics
Compte Rendu 131	1971	No	Small Particles in Glass
Chemiker Zeitung 571	1972	Yes	Photochromic Glass
Feinwerk & Micronic 52	1973	No	Photochromic Glass
"Photochromism" 667	1974	No	Photochromic Glass
Applied Physics 1370	1976	Yes	Darkening Kinetics
"Materials Science" 91	1977	No	Photochromic Glass
Phil Mag B 279	1979	Yes	Darkening Kinetics
Kirk Othmer Encycl 121	1979	No	Photochromic Glass
Phys Chem Glasses 115	1979	No	Boron Coordination
Phys.Chem. Glasses 114	1980	yes	Boron Coordination
J. NonXtalline Solids 209	1980	No	Boron Coordination
Phys Chem Glasses, 193	1980	No	Second Order Phase Transitions
Contem Physics 77	1980	No	Photochromic Glasses
Contemporary Physics 77	1980	No	Photochromic Glasses
Phy. Chem. Glasses 6	1981	Yes	Theoretical Structure of Glass
J.NonXtalline Solids 217	1981	No	Relaxing Abe Rule
Phil Mag B 453	1981	Yes	Darkening Kinetics
Ency of Science & Eng	1981	No	Photochromic Glass
J.NonXtalline Solids 69	1982	No	Ophthalmic Photochromic Glass
Phys Chem Glasses 108	1982	Yes	Boron Coordination
JNonXtalline Solids 257	1983	No	Phase Separation
JNonXtalline Solids 201	1983	No	Alkali Borates
Phil Mag B 331	1984	Yes	Stabilization of Fermi Level
Phys & Chem Glasses 91	1984	No	Temperature Dependence of Darkening
J. Chem. Ed 472	1985	No	Photochromic Glass
JNonXtalline Solids 227	1985	No	Quench Rate and Color
"Amorphous Solids" 13	1986	No	Chemical Disorder
"Commercial Glasses" 151	1986	No	Photosensitive Glasses
JNonXtalline Solids 141	1986	No	Viscosity and Structure

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JNonXtalline Solids 251	1986	No	Influence of Silica on Boron Coord
Encyl of Phys Science 425	1987	No	Photochromic Glass
Lightwave Technology 197	1988	No	Hydrogen Aging of Optical Fibers
Glasstechnische Berichte 72	1988	Yes	Density and Boron Coordination
JNonXtalline Solids 301	1989	No	Entropy of Mixing
JNonXtalline Solids 326	1991	No	Calc of Density of Peroxyls
"Optical Properties of Glass" 125	1991	Yes	Photochromic Glass
SPIE vol 1590 138	1991	Yes	Radiation Induced Optical Effects
Applied Optics 5221	1992	No	Colorless High Silver Glasses
JNonXtalline Solids 70	1993	No	Interdiffusion
High Temperature Science 51	1993	No	Interactions of Polyvalent Ions in Melt
SPIE vol 2287 144	1994	No	Ppt of Copper Halides
SPIE vol 2287 144	1994	Yes	Optical Properties of Stretched Glass
Phys Chem Glasses 131	1995	No	Basicity and Redox in Silicate Melts
Applied Phys Letters 584	1996	Yes	Optical Properties of CuO
SPIE CR64 40	1996	No	Inorganic Optical Materials
JNonXtalline Solids 164	1996	No	Oxygen Vacancies in Silica
JNonXtalline Solids 154	1996	Yes	Sodium Redistribution between oxide phases
Molecular Crystals 1	1997	No	Inorganic Photochromic Systems
JNonXtalline Solids 25	1997	No	Boron - Oxygen Bonding
JNonXtalline Solids 53	1998	No	Influence of Host on CuX Ppt
SPIE vol 3424	1998	Yes	Induced Absorption in Silica
J. Chem. Ed. 1490	1998	No	Thermodynamic Potential Functions
Applied Optics 5778	2000	Yes	Transient Absorption in Silica
JNonXtalline Solids 262	2003	Yes	Ion Exchange Equilibria